Entropy and Potential Temperature

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ABSTRACT

The theoretical investigations presented in this paper show that the various definitions of potential temperatures, such as the potential temperature of dry air and of moist air, the equivalent potential temperature, the liquid water potential temperature, the ice-liquid water potential temperature and the wet equivalent potential temperature can be unified by one single definition. This general potential temperature is named the entropy temperature as it is a measure of entropy. The entropy state function for a system of cloudy air and the entropy budget are presented and discussed. For each of the potential temperatures the respective thermodynamic equation for which the potential temperature is an integral of the form, θ = constant, is reviewed on the basis of the entropy concept. As one result, it is found that the ice-liquid water potential temperature θ_{il} is only an integral of the corresponding thermodynamic equation if saturation or chemical equilibrium between water vapor and liquid water or ice is assumed. A prognostic equation for the entropy temperature is derived using the entropy budget equation. This equation describes irreversible effects and holds also for an open system. From this equation exact prognostic equations for each of the potential temperatures can, at least in principle, be derived.

1. Introduction

The formulation of the basic thermodynamic equation and the definition of appropriate thermodynamic variables to be used in numerical cloud models has been discussed in quite a number of papers over the last two decades, e.g., Das (1969), Betts (1973), Deardorff (1976), Wilhelmson (1977), Lipps and Hemler (1980), Tripoli and Cotton (1980, 1981) and Pointin (1984). The objective was to find suitable methods to treat thermodynamic processes in clouds under saturated or unsaturated conditions with the ice phase being involved. Another aim was to derive physical quantities in terms of potential temperatures which are conserved under the various processes considered. The procedures used in the various papers were almost identical. First, the basic thermodynamic equation was simplified by specific assumptions and approximations. Then a potential temperature θ was defined, which is an integral of the thermodynamic equation of the form θ = constant as sketched in the lower part of Fig. 1. Generally, a closed system is assumed and irreversible fluxes are ignored.

If the system consists only of dry air, the potential temperature $\theta = T(p/p_0)^{-R_0/c_{p0}}$ is a constant. If water vapor is included, the potential temperature θ_m of moist air is constant, where θ_m is defined similarly to θ. Lipps and Hemler (1980) discussed several forms of the thermodynamic equations and their solutions, especially the equivalent potential temperature. It is a constant in a closed parcel of cloudy air under saturated adiabatic motions. It can be approximated to yield the liquid-water potential temperature which, however, is slightly different from the one introduced by Betts (1973). Tripoli and Cotton (1981, hereafter referred to as TC) extended the definition of liquid water potential temperature to include the ice phase. They defined an ice–liquid water potential temperature, which they considered to be conserved even under nonequilibrium conditions. It is one objective of this paper to check the derivation of ice–liquid water potential temperature and to clarify its conservation properties. A further potential temperature was defined by Pointin (1984). His wet equivalent potential temperature was considered to be essentially constant under various transformations, including phase changes. Although the various potential temperatures are constant only if the system is closed and if irreversible fluxes are ignored, it is commonly hoped that these quantities remain nearly constant if the system is assumed to be open and if irreversible fluxes are allowed.

One general remark can be made. All attempts in deriving conservative quantities are based on the first law of thermodynamics and the Gibbs equation. Thus, the differences can only arise from the different assumptions and approximations made subsequently. This will be shown in this paper when several definitions of potential temperatures will be reviewed based on the Gibbs equation.

Using the Gibbs equation and the first law of thermodynamics it is possible to derive a budget equation for the entropy, which also includes mass and energy exchanges and other fluxes through the system's boundaries (De Groot and Mazur, 1969). The second

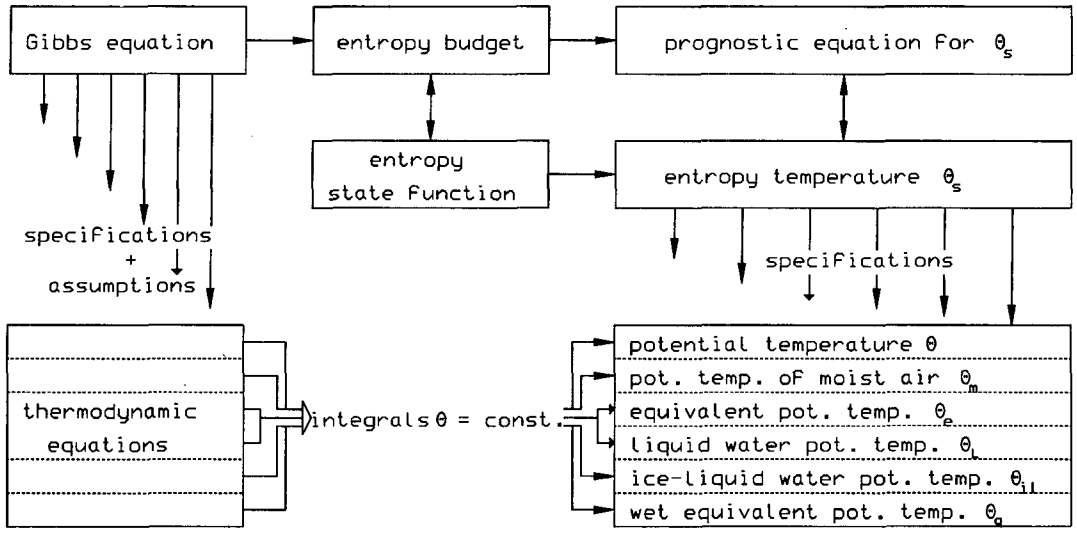

FIG. 1. Principal sketch of derivations and relations between entropy, entropy temperature and the various definitions of potential temperature.

law of thermodynamics expresses the positive definiteness of the entropy sources. Entropy is a function of pressure p, temperature T and concentrations m^k, as will be discussed later on in this paper, and, therefore, is a state function. As the entropy budget is strongly related to the Gibbs equation which serves as the originator for the various thermodynamic equations used in atmospheric physics, it is a straightforward attempt to look for the relations between the various potential temperatures, which are solutions of corresponding thermodynamic equations and entropy. It is the objective of this paper to clarify this relation. The result is that the various definitions of potential temperatures can be unified by a single one which we call entropy temperature θ_s. Its definition [see Eq. (3.23)] mainly involves the entropy state function and, therefore, it can be regarded as a direct measure of entropy, thus justifying the name entropy temperature. The existence of the entropy budget enables us to derive a prognostic equation for the entropy temperature which includes irreversible processes and which also holds for an open system. The procedure so far is sketched in the upper half of Fig. 1. The general character of the entropy temperature can now be demonstrated in a unique way. We apply a set of well-defined assumptions and approximations to the Gibbs equation, as well as to the entropy temperature. The application to the Gibbs equation results in the various thermodynamic equations discussed by many authors, e.g., by Lipps and Hemler (1980). The solutions to these equations are of the form θ = constant where θ is one of the potential temperatures considered in the following. The method is illustrated in the left and in the lower half of Fig. 1. If we now apply the same set of assumptions and approximations to the analytical expression for the entropy temperature (right half of Fig. 1) it reduces

- to the definition of potential temperature θ in the case of dry air,
- to the definition of potential temperature of moist air θ_m in a mixture of dry air and water vapor,

and if some additional approximations are made

- to the definition of equivalent potential temperature θ_e for a saturated 'warm' cloud,

and under the respective conditions discussed later

- to the definition of liquid water potential temperature θ_L,
- to the definition of ice–liquid water potential temperature θ_{il},
- to the wet equivalent potential temperature θ_q.

It is one major finding of this paper that such a general potential temperature exists and that an analytical expression for it can be given. Because of its general nature, the prognostic equation for θ_s can also be used to derive exact formulations of prognostic equations for the various potential temperatures, including irreversible fluxes and assuming an open system. Obviously, the fact that the various potential temperatures can be unified by the entropy temperature, which is more or less a measure of entropy, stresses the importance of entropy in atmospheric thermodynamics. It also raises the question of how entropy can be used in cloud modeling. This and the practical consequences of having found a general potential temperature are discussed in section 5. Our emphasis in this paper, however, is placed on the theory. For that purpose we have to presume a clear and precise description of the basic equations, the terminology, the considered system and the various approximations made; this is done in section 2. The theory is based on the Gibbs equation,

the entropy budget and the entropy state function, all of which we assume to be given. For a detailed discussion of their derivation and relation to each other we refer to the textbook of De Groot and Mazur (1969) and on the papers of Herbert (1973a,b, 1975). A short presentation of the entropy state function, the Gibbs equation and the entropy budget is given in section 3. The definition of entropy temperature θ_s and its prognostic equation can also be found there. In section 4 we review the various derivations of potential temperatures on the base of the entropy concept and relate them to the entropy temperature. The temperatures considered are the potential temperature θ of dry air, of moist air θ_m, the equivalent potential temperature θ_e, the liquid water potential temperature θ_L, the ice–liquid water potential temperature θ_{il} and the wet equivalent potential temperature θ_q.

In this review, assumptions and approximations are presented in a new light and new information is yielded, especially for TC's ice–liquid water potential temperature. Summary, conclusions and applications of the findings follow in section 5.

2. Assumptions, definitions and basic equations

We consider a volume of cloudy air consisting of four partial masses: the mass of dry air M^0, the mass of water vapor M^1, the mass of liquid water M^2 and the mass of ice M^3. This volume, which is also denoted a *system* of cloudy air, contains the total mass M:

$$M = M^0 + M^1 + M^2 + M^3. \tag{2.1}$$

After division by M we get constraints for the concentrations $m^k = M^k/M$

$$1 = m^0 + m^1 + m^2 + m^3, \tag{2.2}$$

and for their differential changes dm^k

$$0 = dm^0 + dm^1 + dm^2 + dm^3. \tag{2.3}$$

Changes of concentration m^k may be caused by exchange of mass through the system boundaries, which is called *external* change $d_e m^k$, or by an *internal* change due to phase transitions $d_i m^k$ with

$$dm^k = d_e m^k + d_i m^k. \tag{2.4}$$

The internal change $d_i m^k$ defines the phase flux

$$J^k = \frac{d_i m^k}{dt}. \tag{2.5}$$

It follows that

$$d_i m^0 = 0, \quad d_i m^1 + d_i m^2 + d_i m^3 = 0. \tag{2.6}$$

How are the partial masses distributed over the volume? We assume that both dry air and water vapor are ideal gases with constant specific heats. Both gases are ideally mixed. This implies that each of them behaves as if the other one is not present. The assumption of an ideal mixture also has direct implications for the free energy of the system and consequently, for the entropy. This will be considered in the next section. In contrast to the gases, liquid water and ice do not mix either with each other or with the gases. They exist in pure form. All liquid water is assumed to appear in one big drop. If a drop spectrum should be created, work has to be done to split the drop in smaller droplets and mix them with the ambient moist air. This would lead to an additional mixing entropy. If all liquid water is partitioned in drops and if these drops are as small as water molecules, all liquid water would have been evaporated and a corresponding amount of entropy would have been created. But in our model concept we totally ignore the existence of individual drops of different size and all related physical effects. Thus, all effects like curvature effect, kinetic effect, internal circulation in the drops, temperature difference between drops and ambient air, radius dependent fall speeds, etc., are ignored.

The system must be small enough so that homogeneity can be assumed within it, with vanishing temperature and pressure gradients $\nabla T = 0$, $\nabla p = 0$. Mathematically the system is treated as infinitesimally small. It should, however, be large enough that continuum physics can be applied to it and that temperature and pressure, as well as entropy, are well defined and meaningful quantities. We therefore assume the atmosphere to be in thermal and mechanical equilibrium locally. Of course, this does not hold globally, thus allowing for larger scale heat fluxes and pressure gradient forces.

Each partial mass has one uniform partial velocity $\mathbf{V}_k$. The velocity of the system is defined as the velocity of the center of mass

$$\mathbf{V} = \mathbf{V}_n m^n = \mathbf{V}_0 m^0 + \mathbf{V}_1 m^1 + \mathbf{V}_2 m^2 + \mathbf{V}_3 m^3. \tag{2.7}$$

It should be noted that, for convenience, Einstein's summation convention is used as illustrated in (2.7), when indices n or m appear twice in the same expression. The motion relative to the system's velocity is defined as *diffusion velocity* $\mathbf{V}'_k$

$$\mathbf{V}'_k = \mathbf{V}_k - \mathbf{V}, \tag{2.8}$$

and the corresponding mass flux is called *diffusion flux*

$$\mathbf{J}^k = \rho m^k \mathbf{V}'_k, \tag{2.9}$$

where ρ is the total density of the system. The sum of all diffusion fluxes vanishes

$$\mathbf{J}^0 + \mathbf{J}^1 + \mathbf{J}^2 + \mathbf{J}^3 = 0. \tag{2.10}$$

The expressions $\mathbf{J}^1$, $\mathbf{J}^2$ and $\mathbf{J}^3$ may be thought of as the diffusion fluxes of water vapor, rain and precipitating ice, respectively. Diffusion fluxes, as defined here, transport mass through the boundaries of the volume under consideration and change the concentration of the respective partial mass. The diffusion fluxes do not change the total mass of the system, cf. Eq. (2.10). It should be noted that all diffusion fluxes are assumed

to be irreversible fluxes and that the definition of the diffusion flux with Eqs. (2.7)–(2.9) represents one possible definition. Other definitions and their implications are treated by Herbert (1980, 1983) in much detail. It is found that the entropy budget depends strongly on the definition of the diffusion fluxes.

The description of the system is given in such detail for various reasons. First, it should be noted that the assumptions and restrictions are not a special feature of this paper but are very common. They are, for example, used in the papers of Betts (1973), Deardorff (1976), Lipps and Hemler (1980), Tripoli and Cotton (1980, 1981) and Pointin (1984), which are referred to very often in this paper. All theories concerning adiabats (see for instance the textbook of Dutton, 1976) make use of these assumptions. This also holds for all numerical cloud models where cloud microphysics is treated in parameterized form. Thus, for clarification, it is worthwhile to depict in detail the assumptions and idealizations of the system by which the cloud is described.

The ignorance of all effects related to the existence of individual drops has several reasons. Mainly, it is of preliminary character, which means that the assumptions are made for reasons of simplicity and that further studies will not make use of them. We also note that the water substances appear in pure form and, consequently, for example, the effect of salt soluted in drops is ignored. As it is one objective of this paper to review various definitions of potential temperatures and to compare them with the entropy, it should be kept in mind that identical assumptions have to be considered.

Each function of p, T, m^k exclusively is called a *state function.* Any extensive state function $\Psi = \Psi(p, T, M^k)$ can be put in the form

$$\Psi = \psi_n M^n \quad \text{or} \quad \psi = \psi_n m^n, \tag{2.11}$$

where $\psi = \Psi/M$ and $\psi_k = \partial\Psi/\partial M^k|_{p,T}$ are the specific values of Ψ. A state function is called *extensive* if it is a homogeneous function of first order in the partial masses M^k. In contrast, pressure p and temperature T are *intensive* functions, which are homogeneous functions of order zero in M^k. With the aid of Eq. (2.11) and using the total water concentration m^t

$$m^t = m^1 + m^2 + m^3, \tag{2.12}$$

Eq. (2.11) reads as

$$\psi - \psi_0 m^0 = \psi_2 m^t + (\psi_1 - \psi_2) m^1 + (\psi_3 - \psi_2) m^3. \tag{2.13}$$

It is further assumed that the volume occupied by liquid water and ice is small compared with those of the gases dry air and water vapor, and thus the specific volumes v_2 and v_3 can be ignored in the equation of state.

3. Entropy and entropy temperature

In this section we present an analytical expression for the entropy state function and subsequently derive a budget equation for the entropy on the basis of the Gibbs equation for a system of cloudy air. We discuss the entropy budget by briefly illustrating the various terms. We then define the entropy temperature on the base of the entropy state function and derive a prognostic equation for it. In the following, we refer very closely to the formulation and theory laid down by Hinkelmann[1] and Herbert (1973a,b, 1975) which can be found in similar form in the textbook of De Groot and Mazur (1969). Therefore, derivations of some of the following equations are omitted and can be found in these or other publications (e.g., Iribarne and Godson, 1973; Dutton, 1976).

a. The entropy state function

We look for an expression of the form (2.11) for the entropy s:

$$s = s_n m^n, \tag{3.1}$$

which means that we have to specify the partial entropies s_k for the system previously defined. Therefore, we have to specify

- s_0 the entropy of dry air in the ideal mixture of moist air,
- s_1 the entropy of water vapor in the ideal mixture of moist air,
- s_2 the entropy of liquid water in pure phase,
- s_3 the entropy of ice in pure phase.

The entropy for any ideal gas in nonmixed form is found to be

$$s_i = c_{pi} \ln T/T_0 - R_i \ln p/p_0 + s_i^0 \tag{3.2}$$

where R_i is the individual gas constant, c_{pi} is the specific heat at constant pressure for the component i; T_0 and p_0 denote reference values of T and p, and s_i^0 is the value of s_i at this reference point. If, as in our case, dry air ($i = 0$) and water vapor ($i = 1$) are mixed, an additional mixing term $-R_i \ln n^i$ arises in both expressions (3.2) for the partial entropies s_0 and s_1. Thus, we have

$$s_0 = c_{p0} \ln \frac{T}{T_0} - R_0 \ln \frac{p}{p_0} - R_0 \ln n^0 + s_0^0,$$

$$s_1 = c_{p1} \ln \frac{T}{T_0} - R_1 \ln \frac{p}{p_0} - R_1 \ln n^1 + s_1^0, \tag{3.3}$$

where the molar fraction n^i is defined as

$$n^i = \frac{R_i m^i}{R_0 m^0 + R_1 m^1} \quad i = 0, 1. \tag{3.4}$$

The additional terms represent the amount of entropy needed to mix both gases. By mixing, entropy is raised. Remembering that the partial pressure p^i is related to the total pressure by

[1] Unpublished lecture notes.

$$p^i = n^i p, \quad i = 0, 1 \tag{3.5}$$

and therefore

$$p^1 + p^2 = p, \tag{3.6}$$

we rewrite (3.3)

$$s_0 = c_{p0} \ln T/T_0 - R_0 \ln p^0/p_0 + s_0{}^0$$
$$s_1 = c_{p1} \ln T/T_0 - R_1 \ln p^1/p_0 + s_1{}^0. \tag{3.7}$$

As we have assumed that liquid and solid water appear as pure substances we find for their partial entropies

$$s_2 = c_2 \ln T/T_0 + s_2{}^0$$
$$s_3 = c_3 \ln T/T_0 + s_3{}^0. \tag{3.8}$$

Inserting now the partial entropies s_0, s_1, s_2 and s_3 in (3.1), we find

$$s = c_p \ln T/T_0 - R_0 m^0 \ln p^0/p_0 - R_1 m^1 \ln p^1/p_0 + s(0). \tag{3.9}$$

The total specific heat at constant pressure is

$$c_p = c_{pn} m^n = c_{p0} m^0 + c_{p1} m^1 + c_2 m^2 + c_3 m^3,$$

and $s(0) = s_n{}^0 m^n$ is the entropy reference value which is a mass-weighted average of the partial zero-entropies $s_i{}^0$ and thus is not a constant. According to (3.9) it represents the entropy of the system of cloudy air at reference temperature T_0 and reference pressure p_0 if each of the two gaseous components would occupy the whole volume alone. The values of the zero-entropies have to be determined experimentally or by quantum statistical considerations. By this it is found that for T_0 = 273.15 K and p_0 = 1000 mb,

$$s_0{}^0 = 6775 \quad [\text{Ws (K kg)}^{-1}]$$
$$s_1{}^0 = 10320 \quad [\text{Ws (K kg)}^{-1}]$$
$$s_2{}^0 = 3517 \quad [\text{Ws (K kg)}^{-1}]$$
$$s_3{}^0 = 2296 \quad [\text{Ws (K kg)}^{-1}].$$

We note that from $\mu = h - Ts$ and with

$$\left.\begin{aligned} l_{ij} &= h_j - h_i \\ a_{ij} &= \mu_i - \mu_j \end{aligned}\right\}, \quad i,j = 1,2,3, \tag{3.10}$$

it follows that

$$s_k - s_1 = -\frac{l_{k1} + a_{k1}}{T}, \quad k = 2,3 \tag{3.11}$$

holds. The differences of the partial entropies are related to the latent heats l_{ij} and the affinities a_{ij}, which are defined as the differences of the specific enthalpies h_k, and of the specific Gibbs functions μ_k, respectively. The affinities can be determined within the framework of classical thermodynamics for the system of cloudy air previously described and additionally ignoring metastable states such as supercooled water:

$$a_{21} = R_1 T \ln \frac{p^{21}}{p^1}$$
$$a_{31} = R_1 T \ln \frac{p^{31}}{p^1}$$
$$a_{32} = a_{31} - a_{21} = R_1 T \ln \frac{p^{31}}{p^{21}}, \tag{3.12}$$

where $p^{21} = p^{21}(T)$ and $p^{31} = p^{31}(T)$ are the saturation pressures over a plane surface of water or ice, respectively. Equations (3.11) and (3.12) also hold at the reference point and therefore the zero-entropies are not independent of each other, but are related by these equations.

The entropy state function (3.9) can also be put in the form of Eq. (2.13):

$$s - s_0 m^0 = s_2 m^t + \frac{l_{21} + a_{21}}{T} m^1 - \frac{l_{32} + a_{32}}{T} m^3. \tag{3.13}$$

For given values of m^k, p and T, the entropy can be calculated. This state function serves as a basis for deriving the various potential temperatures. In the next section we present a budget equation for entropy which can be derived from the Gibbs equation.

b. The Gibbs equation

The Gibbs equation in its general form for a system of cloudy air is

$$Tds = dh - vdp - \mu_n dm^n, \tag{3.14}$$

where s is the specific entropy, h is the specific enthalpy, v the specific volume and μ_i is the chemical potential of the component i. In an adiabatic system we assume that no heat is added by inner heat fluxes $\mathbf{J}_i{}^q$ or by mechanical energy dissipation $\mathbf{J}..\nabla\mathbf{V}$, where $\mathbf{J}$ is the viscous momentum flux. This assumption implies

$$d_i h - vdp = -\frac{1}{\rho}\nabla \cdot \mathbf{J}_i{}^q dt + \frac{1}{\rho}\mathbf{J}..\nabla\mathbf{V}dt = 0 \tag{3.15}$$

where $d_i h$ denotes the internal change of enthalpy. If we subtract Eq. (3.15) from (3.14), we find the Gibbs equation for an adiabatic system:

$$Tds = -\mu_n dm^n - \frac{1}{\rho}\nabla \cdot (h_n \mathbf{J}^n)dt = -\mu_n dm^n + d_e h. \tag{3.16}$$

We note that the adiabatic assumption does not exclude diffusive fluxes through the system's boundaries. If, however, we close the system we find the Gibbs equation for a closed, adiabatic system:

$$Tds = -\mu_n d_i m^n. \tag{3.17}$$

The difference between reversible and adiabatic conditions should be noted. Reversibility means that all irreversible fluxes vanish, which is a stronger assumption than the adiabatic.

c. The entropy budget

Based on Gibbs' fundamental equation and the first law of thermodynamics, a budget equation for entropy can be derived (Herbert, 1973a; DeGroot and Mazur, 1969). In its most rigorous form the entropy budget reads as

$$\frac{\partial \rho s}{\partial t}+\nabla\cdot(\rho s\mathbf{V})+\nabla\cdot[(\mathbf{J}^q-\mu_n\mathbf{J}^n)/T]$$
$$=-\mu_n J^n/T-\mathbf{J}^n\cdot\nabla(\mu_n/T)-\frac{1}{T^2}\mathbf{J}^q\cdot\nabla T+\frac{1}{T}\mathbf{J}..\nabla\mathbf{V}, \quad (3.18)$$

where $\mathbf{J}^q$ is the heat flux and J^i is the phase flux of the ith component. The nonadvective flux $\mathbf{F}_s$ of entropy is

$$\mathbf{F}_s=\mathbf{J}^q/T-\mu_n\mathbf{J}^n/T=1/T[\mathbf{J}_i^q+(h_n-\mu_n)\mathbf{J}^n]$$
$$=\mathbf{J}_i^q/T+s_n\mathbf{J}^n, \quad (3.19)$$

a sum of the heat flux $\mathbf{J}^q$ and the diffusive fluxes $\mu_n\mathbf{J}^n$ divided by T. The divergence of the sum of advective flux $\rho s\mathbf{V}$ and nonadvective flux $\mathbf{F}_s$ contribute to local changes of entropy. The heat flux $\mathbf{J}^q$ consists of the commonly used inner heat flux $\mathbf{J}_i^q$ and a diffusion flux of enthalpy

$$\mathbf{J}^q=\mathbf{J}_i^q+h_n\mathbf{J}^n.$$

The latter can be combined with the diffusion flux $-\mu_n\mathbf{J}^n$ to yield the entropy diffusion flux $s_n\mathbf{J}^n$ appearing on the r.h.s. of Eq. (3.19). This means that entropy can be changed through the boundaries of the system by either material fluxes, caused by advection $\rho s\mathbf{V}$ or by diffusion $\mathbf{J}^n s_n$, or by the immaterial heat flux $\mathbf{J}_i^q/T$. Heat flux and diffusion flux are both irreversible fluxes, as will be discussed below. The entropy source Q_s is

$$TQ_s=-\mu_n J^n-T\mathbf{J}^n\cdot\nabla(\mu_n/T)-\frac{1}{T}\mathbf{J}^q\cdot\nabla T+\mathbf{J}..\nabla\mathbf{V}. \quad (3.20)$$

The second law of thermodynamics states that $Q_s \geqslant 0$. For reversibility, all irreversible fluxes vanish and we have $Q_s = 0$. Each term of the entropy source is a product of an irreversible flux and its corresponding driving force. The determination of the irreversible fluxes as functions of p, T, m^k and $\mathbf{V}$, which is known as the parameterization of the fluxes, is a crucial point of irreversible thermodynamics. Based on the nonnegativity of the entropy source and using linear Onsager-theory and the principle of Curie, Herbert (1973a) could derive a parameterization theory for all irreversible fluxes appearing in (3.20) on the micro- or molecular scale. Obviously, the parameterization of the irreversible fluxes is a necessary presumption for any application in a cloud model. However, a complete description of the parameterization theory is clearly beyond the objective of this paper as we are mainly concerned here with the principle relations between entropy and the various definitions of potential temperatures. Irreversible fluxes are treated in this paper as well-defined, but open or undetermined quantities. We did not want to exclude them a priori as we do not want to confine ourselves to the restrictive condition of reversibility. We also do not want to get involved with the problems and weaknesses of parameterization schemes such as the scale dependency, the closure problem of turbulent fluxes, and the radius dependency of precipitation fluxes, to name but a few. We consider the irreversible fluxes as known functions, at least in principle.

An alternative form of the entropy budget is

$$\frac{\partial \rho s}{\partial t}+\nabla\cdot\rho s\mathbf{V}+\frac{1}{T}\nabla\cdot\mathbf{J}_i^q$$
$$+\frac{1}{T}\nabla\cdot[T(s_0-s_1)\mathbf{J}^0-(l_{21}+a_{21})\mathbf{J}^2-(l_{31}+a_{31})\mathbf{J}^3]$$
$$=\frac{1}{T}(-a_{21}J^2-a_{31}J^3+\mathbf{J}..\nabla\mathbf{V})-\mathbf{J}^0\cdot\nabla(\mu_0-\mu_1)$$
$$-\mathbf{J}^2\cdot\nabla a_{21}-\mathbf{J}^3\cdot\nabla a_{31}, \quad (3.21)$$

where the inner heat flux $\mathbf{J}_i^q$ is used and l_{21} and l_{31} denote the latent heats of vaporization and sublimation, respectively. It should be noted that the diffusion flux and the heat flux both contribute to the nonadvective flux, as well as to the entropy source. An entropy change by a nonadvective flux implies simultaneous entropy production by the same flux.

If reversibility is assumed, Eq. (3.18) simplifies to

$$\frac{\partial \rho s}{\partial t}+\nabla\cdot\rho s\mathbf{V}=0, \quad (3.22)$$

or, with the equation of continuity, to

$$\rho ds/dt=0,$$

which means that entropy is conserved in a parcel of air. For such a situation entropy seems to be an appropriate variable to be used in numerical models. Note in (3.21) that under the assumption of chemical equilibrium in a cloud the affinity $a_{21} = 0$ vanishes, but a phase flux J^2 is still allowed. This flux, however, must then be interpreted as a reversible flux. The phase changes under chemical equilibrium do not produce entropy.

In conclusion, it can be stated that a budget equation for entropy exists, that the various terms have a well-defined meaning and that they can be written as functions of the independent variables. The budget equation reduces for reversibility to a very simple form and entropy is conserved. Entropy is still conserved if reversible phase changes or fluxes are allowed.

d. The entropy temperature

Entropy is a quantity which is not often used in meteorology. To make us more familiar with entropy,

we express entropy in terms of a temperature, which we call entropy temperature θ_s. It is defined by

$$\theta_s = T_0 \exp\left(\frac{s - s^* m^0}{c^* m^0}\right) \tag{3.23}$$

where

$$s^* = s_0{}^0 + s_2{}^0 r^t$$
$$c^* = c_{p0} + c_2 r^t \tag{3.24}$$

denote some kind of zero entropy and specific heat, respectively. If the entropy state function is inserted into (3.23) we find

$$\theta_s = T(p^0/p_0)^{-R_0/c^*} \times \exp[(l_{21} + a_{21})r^1/c^*T - (l_{32} + a_{32})r^3/c^*T]. \tag{3.25}$$

We can also use Eq. (3.25) as the definition for θ_s, but we preferred Eq. (3.23) to stress the close relationship between entropy and entropy temperature. It is the objective of this paper to show that the various potential temperature definitions known in the literature can be unified by the above definition of entropy temperature. It should be noted that the definition of entropy temperature presumes a system of cloudy air and especially the existence of liquid water, as can be seen from Eq. (3.24). Problems arise if no liquid water is present, either locally or in principle. Parts of this problem will be treated in the following. It was already suggested by Paluch (1979) to define a potential temperature on the base of the specific entropy. However, her definition of wet equivalent potential temperature was restricted to a pure water cloud. It was later extended by Pointin (1984) to account for ice (cf. section 4 f).

e. A prognostic equation for the entropy temperature

Due to the simple relation (3.23) between entropy and entropy temperature, and due to the existence of an entropy budget, it is a straightforward exercise to derive a prognostic equation for the entropy temperature. Differentiating (3.23) with respect to time and using (3.24) and the continuity equation of dry air we find a prognostic equation for the entropy temperature

$$\rho m^0 c^* d \ln\theta_s/dt = D\rho s/Dt + [(s_0{}^0 - s_2{}^0) + (s - s^* m^0)(c_{p0} - c_2)/(c^* m^0)]\nabla \cdot \mathbf{J}^0. \tag{3.26}$$

In this equation

$$\frac{D\rho s}{Dt} = \frac{\partial \rho s}{\partial t} + \nabla \cdot \rho s \mathbf{V} = \rho \frac{ds}{dt}$$

has to be replaced by the budget equation for entropy s. If we use Eq. (3.18), we find

$$\rho m^0 c^* \mathrm{d} \ln\theta_s/dt - [(s_0{}^0 - s_2{}^0) + (s - s^* m^0)(c_{p0} - c_2)/(c^* m^0)]\nabla \cdot \mathbf{J}^0 + \nabla \cdot [(\mathbf{J}^q - \mu_n \mathbf{J}^n)/T] = -\mu_n J^n/T - \mathbf{J}^n \cdot \nabla(\mu_n/T) - \frac{1}{T^2}\mathbf{J}^q \cdot \nabla T + \frac{1}{T}\mathbf{J}..\nabla \mathbf{V}, \tag{3.27}$$

and with Eq. (3.21) we similarly obtain

$$\rho m^0 c^* d \ln\theta_s/dt - [(s_0{}^0 - s_2{}^0) + (s - s^* m^0)(c_{p0} - c_2)/(c^* m^0)]\nabla \cdot \mathbf{J}^0 + \frac{1}{T}\nabla \cdot \mathbf{J}_i^q + \frac{1}{T}\nabla \cdot [T(s_0 - s_1)\mathbf{J}^0 - (l_{21} + a_{21})\mathbf{J}^2 - (l_{31} + a_{31})\mathbf{J}^3] = \frac{1}{T}(-a_{21}J^2 - a_{31}J^3 + \mathbf{J}..\nabla \mathbf{V}) - \mathbf{J}^0 \cdot \nabla(\mu_0 - \mu_1) - \mathbf{J}^2 \cdot \nabla a_{21} - \mathbf{J}^3 \cdot \nabla a_{31}. \tag{3.28}$$

Both equations are equivalent. Either (3.27) or (3.28) represents the most general prognostic equation for θ_s under the general assumptions given in section 2. It is also valid for an open system and includes irreversible fluxes and is thus neither restricted to a closed system nor to the assumptions of adiabasy or reversibility.

Entropy temperature θ_s is related to entropy by the functional relationship (3.23), and thus can be considered as a measure of entropy. However, Eq. (3.23) involves, besides entropy, the concentration of dry air m^0 and the total water mixing ratio r^t. Therefore, a constant entropy does not generally imply that the entropy temperature is also a constant. Equation (3.26) shows that the main difference between the individual time derivative $d\theta_s/dt$ and the budget operator $D\rho s/Dt$ is related to the divergence term $\nabla \cdot \mathbf{J}^0$. The diffusion flux $\mathbf{J}^0$ of dry air vanishes if the dry air moves with the center of mass velocity. This is the case if the system consists only of dry air or if it is closed, or if reversibility is assumed. If one of these conditions is met, changes of entropy temperature can be caused by entropy changes alone:

$$\rho m^0 c^* d \ln\theta_s/dt = D\rho s/Dt, \tag{3.29}$$

independent of further approximations. We also should note that $d\theta_s/dt = 0$ if reversibility is assumed. Then θ_s remains constant for any parcel of cloudy air.

In summary, we would like to point out the importance of the prognostic equation for the entropy temperature as it holds for an open system and describes the irreversible fluxes of the phase changes J^i, diffusion $\mathbf{J}^i$, heat $\mathbf{J}_i^q$ and momentum $\mathbf{J}$. It is correct as long as the entropy budget equation is assumed to be correct. As entropy temperature turns out to be identical with the various other definitions of potential temperature

under the respective conditions (which will be shown in the next section), the prognostic equation for the entropy temperature enables us to derive prognostic equations for each potential temperature, again holding for an open system and including irreversible effects.

4. The relation between entropy and various definitions of potential temperature

Various definitions and derivations of potential temperatures are reviewed and the relation to entropy or entropy temperature is established in this section. Starting from the Gibbs equation for the system under consideration, we first check some assumptions and approximations under which the potential temperatures are constant. We then derive for the same conditions an analytical expression for the entropy temperature and compare it with the definition of the corresponding potential temperature.

The main issue of this section is not to prove the conservation properties of θ, θ_m, θ_e and θ_L once again, as this has been the subject of many papers; rather it is to apply one and the same method to all of the various definitions of potential temperature, thus illustrating the formal and physical relations between each of them and entropy or entropy temperature, respectively.

We restrict ourselves to the presentation of the assumptions, the approximations, and the results, and omit derivations as far as they can be found elsewhere.

a. Potential temperature θ of dry air

The Gibbs equation for a closed adiabatic system of dry air reads as

$$ds = 0. \tag{4.1}$$

With (3.2) and the definition of potential temperature θ

$$\theta = T\left(\frac{p}{p_0}\right)^{-k_0}, \quad k_0 = \frac{R_0}{c_{p0}} \tag{4.2}$$

we find

$$ds = c_{p0}d\ln T - R_0 d\ln p = c_{p0}d\ln\theta = 0, \tag{4.3}$$

which also means that $d\theta = 0$ under these assumptions. Thus, the dry potential temperature θ is constant in a closed, adiabatic system.

If only dry air is considered, the entropy temperature θ_s (3.23) reduces to

$$\theta_s = T_0 \exp\left(\frac{s - s^* m^0}{m^0 c^*}\right) = T_0 \exp\left(\frac{s_0 - s_0{}^0}{c_{p0}}\right)$$
$$= T\left(\frac{p_0}{p}\right)^{R_0/c_{p0}} = \theta, \tag{4.4}$$

and the entropy temperature is equivalent to the potential temperature of dry air. Note that the relation (4.4) is not confined to a closed, adiabatic system but is generally valid for a system of dry air which is open and where irreversible fluxes are acting.

The prognostic equation (3.27) for θ is

$$\rho c_{p0} d(\ln\theta)/dt + \nabla\cdot(\mathbf{J}^q/T) = -\frac{1}{T^2}\mathbf{J}^q\cdot\nabla T + \frac{1}{T}\mathbf{J}..\nabla\mathbf{V}. \tag{4.5}$$

We note that for a system of dry air, the diffusion fluxes as well as the phase fluxes vanish. If all irreversible fluxes vanish, (4.5) reads as

$$\frac{d\theta}{dt} = 0. \tag{4.6}$$

b. Potential temperature θ_m of moist air

We consider a closed adiabatic system of dry air and water vapor. The Gibbs equation together with the entropy state function for dry air and water vapor (3.7) yield:

$$\begin{aligned} 0 = ds &= m^0 ds_0 + m^1 ds_1 + s_0 dm^0 + s_1 dm^1 \\ &= m^0(c_{p0}dT/T - R_0 dp/p - R_0 dn^0/n^0) \\ &\quad + m^1(c_{p1}dT/T - R_1 dp/p - R_1 dn^1/n^1) \\ &= c_p dT/T - (R_0 m^0 + R_1 m^1)dp/p \end{aligned} \tag{4.7}$$

$$\Rightarrow$$

$$d\ln T - (R_0 m^0 + R_1 m^1)/(c_{p0}m^0 + c_{p1}m^1)d\ln p = 0. \tag{4.8}$$

The differentials $dm^0 = dm^1 = 0$ vanish as it is a closed system, and thus $d\ln n^0 = d\ln n^1 = 0$ also vanish. We immediately find θ_m with

$$\theta_m = T\left(\frac{p}{p_0}\right)^{-k_m}, \quad k_m = \frac{R_0 m^0 + R_1 m^1}{c_{p0}m^0 + c_{p1}m^1} \tag{4.9}$$

as an integral of (4.8). Thus, in a closed adiabatic system of moist air, θ_m is constant. Theoretically, θ_m also remains constant in supersaturated conditions as long as condensation is not allowed. In nature, however, condensation would occur and θ_m is not an adequate quantity for saturated or supersaturated conditions.

Before we compare θ_m and the entropy temperature θ_s, a general note should be made. As the definition of θ_s Eqs. (3.23) and (3.24) formally stresses the liquid water constitutent m^2, it implicitly assumes the presence of liquid water in the system. Therefore, it is physically not very meaningful to compare θ_s with quantities that are only defined for dry air or moist air, not including any liquid water. Formally, however, a comparison can be made which can also be successful, as we have seen in the case of potential temperature of dry air θ. The problem can also be put into the question: What is the meaning of the specific heat of water c_2 [in Eq. (3.24)] in a dry or moist system?

If we make the assumption

$$c^* = c_{p0} + c_2 r^t = c_{p0} + c_2 r^1 = (c_{p0} m^0 + c_2 m^1)/m^0 \approx c_{p0} \tag{4.10}$$

for which $m^1 \ll m^0$ is a sufficient condition, we overcome the formal difficulty and find for the entropy temperature θ_s in a system of moist air

$$\theta_s = \theta_m n^{0-R_0 m^0/c_p} n^{1-R_1 m^1/c_p}. \tag{4.11}$$

We recognize that θ_m is a measure of the entropy of a mixture of dry air and moist air, where, however, the entropy contribution due to the mixing of both gases is ignored. Potential temperature θ_m, as defined by (4.9) does not contain the full information about the entropy s. Inserting a realistic value of 0.99 for n^0 in (4.11), the mixing factor can be estimated to $\simeq 1.01$, which means that θ_s and θ_m differ by $\approx 1\%$. We should note that in a closed system m^0 and m^1 are constant and that consequently, θ_s from (4.11) also satisfies Eq. (4.8). However, the definition (4.9) of θ_m does not in general take into account the effect of mixing.

A prognostic equation for θ_m can be derived easily from (3.27) assuming $m^2 = m^3 = 0$, $s^* = s_0{}^0$, $c^* = c_{p0}$ [Eq. (4.10)], $J^0 = 0$, $J^1 = 0$:

$$\rho m^0 c_{p0} d \ln\theta_m/dt - s/m^0 \nabla \cdot \mathbf{J}^0 + \nabla \cdot [(\mathbf{J}^q - \mu_n \mathbf{J}^n)/T]$$

$$= -\mathbf{J}^n \cdot \nabla(\mu_n/T) - \frac{1}{T^2}\mathbf{J}^q \cdot \nabla T + \frac{1}{T}\mathbf{J}\,..\,\nabla \mathbf{V}. \tag{4.12}$$

c. The equivalent potential temperature

We now consider a closed adiabatic system containing dry air, water vapor and liquid water, and assume equilibrium between water vapor and liquid water. Evaluating the Gibbs equation for this system, we find

$$Tds = -\mu_n dm^n = -\mu_0 dm^0 - \mu_1 dm^1 - \mu_2 dm^2.$$

As the system is closed, all dm^k have to be interpreted as inner changes $d_i m^k$. With $d_i m^0$ and $d_i m^1 = -d_i m^2$, we get

$$Tds = -(\mu_2 - \mu_1) dm^2 = -a_{21} dm^2 = 0,$$

because under equilibrium conditions the affinities vanish. Thus, we get $ds = 0$, which means that entropy is constant. Inserting the state function for entropy (3.9), we find, after some algebraic manipulations and using the Clausius–Clapeyron equation

$$\frac{dT}{T} - k_{21}\frac{dp}{p} + d\left(\frac{k_{21} l_{21} r^{21}}{R_0 T}\right) + k_{21} d\left[\ln\left(\frac{R_0}{R_1} + r^{21}\right)\right] = 0, \tag{4.13}$$

where r^{21} is the water vapor saturation mixing ratio. This equation represents the first law of thermodynamics for a closed adiabatic system under chemical equilibrium conditions. It should be noted that

$$k_{21} = \frac{R_0 m^0}{c_{p0} m^0 + c_2 m^t} = \frac{R_0}{c_{p0} + c_2 r^t}$$

is a generalized adiabatic coefficient, and that we presume that liquid water is present: $m^2 \neq 0$.

Equation (4.13) is equivalent to Eq. (1a) in the paper of Lipps and Hemler (1980). The authors discussed in detail numerical solutions of (4.13) and compared them with various approximations of (4.13). However, they did not give an integral. Equation (4.13) is also equivalent to Eq. (1) in the paper of Betts (1973). Integration of (4.13) gives

$$T\left(\frac{p_0}{p}\right)^{k_{21}} \times \exp\left\{k_{21}\left[\frac{l_{21} r^{21}}{R_0 T} + \ln\left(\frac{R_0}{R_1} + r^{21}\right)\right]\right\} = C. \tag{4.14}$$

C is an integration constant which we express as a temperature

$$\theta_e = C \exp[-k_{21} \ln(R_0/R_1)]. \tag{4.15}$$

Inserting C in (4.14) we find that the equivalent potential temperature defined by either (4.14) and (4.15) or by

$$\theta_e = T\left(\frac{p_0}{p}\right)^{k_{21}} \exp\left\{k_{21}\left[\frac{l_{21} r^{21}}{R_0 T} + \ln\left(1 + \frac{R_1}{R_0} r^{21}\right)\right]\right\} \tag{4.16}$$

is a solution of (4.13).

As $\ln[1 + R_1/R_0 r^{21}] = -\ln p^0/p$ holds, we can introduce the partial pressure of dry air p^0 in (4.16) to obtain

$$\theta_e = T\left(\frac{p_0}{p^0}\right)^{k_{21}} \exp\left(k_{21}\frac{l_{21} r^{21}}{R_0 T}\right). \tag{4.17}$$

It also holds that

$$\theta_e = T\left(\frac{p_0}{p^0}\right)^{k_{21}} \exp\left[\frac{l_{21} r^{21}}{(c_{p0} + r^t c_2) T}\right]. \tag{4.18}$$

The equivalent potential temperature is a constant in a closed adiabatic system where water vapor is saturated. If in a rising parcel of cloudy air the liquid water remains in the parcel and does not fall out, then θ_e is constant. It should be noted that other definitions of equivalent potential temperature exist (e.g. Betts, 1973), which arise from approximations of the definition given in this paper. The present one is the most general definition, as no further approximations or assumptions have been made.

We now look for the relation between equivalent potential temperature and entropy temperature. If the cloud is assumed to contain no ice and is in an equilibrium state, we obtain for the entropy temperature θ_s:

$$\theta_s = T(p_0/p^0)^{R_0/(c_{p0} + c_2 r^t)} \exp\left[\frac{l_{21}}{(c_{p0} + c_2 r^t) T} r^{21}\right]$$

$$= T(p_0/p^0)^{k_{21}} \exp\left(\frac{l_{21} k_{21} r^{21}}{R_0 T}\right) = \theta_e. \tag{4.19}$$

As a result, we see that for a saturated "warm" cloud the entropy temperature is identical with the equivalent potential temperature θ_e. Again, a prognostic equation for θ_e can be obtained from Eq. (3.26) with $\theta_s = \theta_e$ and by introducing the equilibrium assumption $a_{21} = 0$.

d. The liquid water potential temperaure θ_L

The liquid water potential temperature θ_L was defined by Betts (1973). Instead of using liquid water concentration m^2 as suggested by Betts, we use the water vapor mixing ratio r^1 or its saturation value r^{21}, respectively, to define the liquid water potential temperature:

$$\theta_L = \theta \exp\left(\frac{l_{21} r^{21}}{c_{p0} T}\right) \tag{4.20}$$

where θ_L as defined with (4.20) is equivalent to the Betts definition in the sense that both satisfy the same thermodynamic equation, Eq. (12) in Bett's paper, if dm^2 is replaced by $-m^0 dr^1$.

θ_L is an approximation of equivalent potential temperature, and we obtain θ_L if we make the following two approximations either in the definition of θ_e or in the differential equation (4.13):

1) $\ln\left(1 + r^{21}\frac{R_1}{R_0}\right) \approx 0 \quad \text{as} \quad r^{21}\frac{R_1}{R_0} \ll 1$

2) $k_{21} = \frac{R_0}{c_{p0} + c_2 r^t} \approx \frac{R_0}{c_{p0}} = k_0.$

It follows that

$$\frac{dT}{T} - k_0 \frac{dp}{p} + d\left(\frac{l_{21} r^{21}}{c_{p0} T}\right) = 0, \tag{4.21}$$

for which Eq. θ_L is a solution. Therefore, liquid water potential temperature θ_L is nearly constant if a closed adiabatic parcel rises under saturation conditions. The error arises from the two approximations made. These approximations are similar but not identical to those leading to Eq. (13) in the paper of Lipps and Hemler (1980). A limit of ±0.5 K was found for the error in θ_e, compared with θ_L made by these approximations. If we apply these approximations to entropy temperature as well as to equivalent potential temperature, the identity (4.19) now reads as

$$\theta_s = \theta_L. \tag{4.22}$$

The entropy temperature equals the liquid water potential temperature.

As in the case of the equivalent potential temperature, we obtain a prognostic equation from (3.26) by using (4.22), the saturation assumption $a_{21} = 0$ and by incorporating the two approximations 1) and 2) which, however, might not be easy to do in a unique way. The derivation of the prognostic equation for the various potential temperatures, therefore, is shown in this paper only in principle.

e. The ice-liquid water potential temperature θ_{il}

In the potential temperatures considered so far, ice was not included. For deep convection models, however, the treatment of ice is essential. One attempt to solve this problem is the use of ice-liquid water potential temperature θ_{il} as defined by Tripoli and Cotton (1981). This temperature is an extension of the liquid water potential temperature θ_L (Betts, 1973), which was previously examined. Tripoli and Cotton (1981, hereafter referred to as TC) based the definition of θ_{il} on an approximated form of the thermodynamic energy equation, and in addition, made some further approximations. It is one objective of this paper to reexamine these approximations in the light of the entropy concept. As we will see, this will clarify some of the error sources connected with these approximations.

TC have discussed the errors in using θ_{il} by comparing it with solutions of the exact thermodynamic equation. They were not aware, however, of the net effect of all approximations and their physical meaning. In the following we derive the differential equation for θ_{il} starting with Gibbs equation (3.17) for a closed adiabatic system ($d\psi \equiv d_i\psi$). We write

$$Tds = -\mu_n dm^n = Tm^n ds_n + Ts_n dm^n.$$

From this it follows that

$$\begin{aligned} Tm^n ds_n &= -(\mu_n + Ts_n) dm^n = -h_n dm^n \\ &= -h_0 dm^0 - h_1 dm^1 - h_2 dm^2 - h_3 dm^3 \\ &= (h_1 - h_2) dm^2 + (h_1 - h_3) dm^3 \\ &= l_{21} dm^2 + l_{31} dm^3. \end{aligned}$$

Dividing by Tm^0 and introducing the mixing ratios we get

$$ds_0 + r^1 ds_1 + r^2 ds_2 + r^3 ds_3 = l_{21}/T dr^2 + l_{31}/T dr^3. \tag{4.23}$$

With the entropy state function (3.9) and with

$$c_{pm} = c_{p0} + r^1 c_{p1} + r^2 c_2 + r^3 c_3 \quad \text{and} \quad R_m = R_0 + R_1 r^1,$$

we find

$$c_{pm} d\ln T - R_m d\ln p + \frac{l_{21}}{T} dr^1 - \frac{l_{32}}{T} dr^3 = 0 \tag{4.24}$$

where the relations $dr^2 + dr^3 + dr^1 = dr^t = 0$ and $l_{32} = l_{31} - l_{21}$ have also been used.

Equation (4.24) is equivalent to TC's Eq. (12). Introducing the potential temperature with (4.2) we get

$$d\ln\theta + \frac{l_{21}}{c_{pm} T} dr^1 - \frac{l_{32}}{c_{pm} T} dr^3 - \left(\frac{R_m}{c_{pm}} - \frac{R_0}{c_{p0}}\right) d\ln p = 0, \tag{4.25}$$

which is TC's Eq. (14).

Next, in TC it was assumed that

$$\frac{R_m}{c_{pm}} - \frac{R_0}{c_{p0}} \approx 0, \tag{4.26}$$

which was expressed as neglection of heat storage by water. This is a crucial assumption, as will be shown. We derive TC's resulting Eq. (15):

$$d\ln\theta + \frac{l_{21}}{c_{p0}T}dr^1 - \frac{l_{32}}{c_{p0}T}dr^3 = 0 \quad \text{[TC Eq. (15)]}$$

from (4.23) by introducing θ and using (3.3):

$$d\ln T - \frac{R_0}{c_{p0}}d\ln p - \frac{R_0}{c_{p0}}d\ln n^0 + \frac{r^1}{c_{p0}}ds_1 + \frac{r^2}{c_{p0}}ds_2 + \frac{r^3}{c_{p0}}ds_3 = -\frac{l_{21}}{c_{p0}T}dr^1 + \frac{l_{32}}{c_{p0}T}dr^3.$$

Now it follows that

$$d\ln\theta + \Delta s = -\frac{l_{21}}{c_{p0}T}dr^1 + \frac{l_{32}}{c_{p0}T}dr^3 \tag{4.27}$$

where

$$\Delta s = -\frac{R_0}{c_{p0}}d\ln n^0 + \frac{r^1}{c_{p0}}ds_1 + \frac{r^2}{c_{p0}}ds_2 + \frac{r^3}{c_{p0}}ds_3.$$

Comparing (4.27) with TC Eq. (15), we see that the assumption (4.26) means that $\Delta s = 0$. This itself means that 1) the mixing term $-R_0/c_{p0}d\ln n^0$ and 2) the expression $m^1ds_1 + m^2ds_2 + m^3ds_3$ have been ignored. Now θ_{il} is introduced by

$$d\ln\theta_{il} = d\ln\theta - \frac{l_{21}}{c_{p0}T}dr^2 - \frac{l_{31}}{c_{p0}T}dr^3 = d\ln\theta - d\left(\frac{l_{21}r^2}{c_{p0}T} + \frac{l_{31}r^3}{c_{p0}T}\right) + \epsilon_1 + \epsilon_2. \tag{4.28}$$

Here r^1 has been replaced by r^2 and r^3.

Now

$$\epsilon_1 = \frac{r^2}{c_{p0}}d\left(\frac{l_{21}}{T}\right)$$

and

$$\epsilon_2 = \frac{r^3}{c_{p0}}d\left(\frac{l_{31}}{T}\right)$$

are ignored to yield θ_{il} as a solution of TC Eq. (15). Using the differentials dr^1 and dr^3, we would find a similar equation to (4.28) for which θ_{eiv} is a solution. Here θ_{il} and θ_{eiv} are defined as

$$\theta_{il} = \theta\exp\left[-\left(\frac{l_{21}(T_0)r^2}{c_{p0}T} + \frac{l_{31}(T_0)r^3}{c_{p0}T}\right)\right]$$

$$\theta_{eiv} = \theta\exp\left[-\left(-\frac{l_{21}(T_0)r^1}{c_{p0}T} + \frac{l_{32}(T_0)r^3}{c_{p0}T}\right)\right], \tag{4.29}$$

where, in addition, l_{21}, l_{31} and l_{32} were taken as constant. We note that besides $\epsilon_1 = 0$ and $\epsilon_2 = 0$ the integrals $\int\epsilon_1 = 0$ and $\int\epsilon_2 = 0$ also vanish, as they do not appear in (4.29).

Altogether, three basic assumptions have been made:

1) $\Delta s = 0 \Leftrightarrow m^1ds_1 + m^2ds_2 + m^3ds_3 = 0$ and $d\ln n^0 = 0$,
2) $\epsilon_1 = 0$ and $\int\epsilon_1 = 0$,
3) $\epsilon_2 = 0$ and $\int\epsilon_2 = 0$.

What is the meaning of these assumptions if they are considered together and not independently of each other? To answer this question we look at the relationship between the latent heat, the affinities and the specific entropies (3.11):

$$\frac{l_{21}}{T} = -\frac{a_{21}}{T} + s_1 - s_2$$

$$\frac{l_{31}}{T} = -\frac{a_{31}}{T} + s_1 - s_3. \tag{4.30}$$

The approximations $\epsilon_1 = 0$ and $\epsilon_2 = 0$ now imply that

$$d\left(\frac{l_{21}}{T}\right) = -d\left(\frac{a_{21}}{T}\right) + ds_1 - ds_2 = 0$$

$$d\left(\frac{l_{31}}{T}\right) = -d\left(\frac{a_{31}}{T}\right) + ds_1 - ds_3 = 0. \tag{4.31}$$

The approximation $\Delta s = 0$ implies that $m^1ds_1 + m^2ds_2 + m^3ds_3 = 0$, which holds for all values of m^1, m^2, m^3. Thus it follows that

$$ds_1 = ds_2 = ds_3 = 0, \tag{4.32}$$

which, inserted in (4.31), means that

$$d\left(\frac{a_{21}}{T}\right) = d\left(\frac{a_{31}}{T}\right) = 0. \tag{4.33}$$

Thus, it is found that the affinities divided by T are constant. Integration yields

$$\frac{a_{21}}{T} = c_1, \quad \frac{a_{31}}{T} = c_2. \tag{4.34}$$

As the integrals $\int\epsilon_1$ and $\int\epsilon_2$ have been omitted, the values of the constants are zero and it follows that

$$a_{21} = a_{31} = 0; \tag{4.35}$$

the affinities themselves vanish. This means that chemical equilibrium exists and that no supersaturation occurs. If all three approximations are taken together, they imply equilibrium conditions. This means that θ_{il} or θ_{eiv} defined with (4.29) is only a solution of the exact thermodynamic equation if and only if saturation is assumed. Thus, it is inconsistent to treat supersaturated cloudy air with θ_{il}.

TC approximated (4.29) empirically by a Taylor's series approximation plus some extra empirical adjustment (Eq. 30 in TC), and then compared it with solutions of the exact thermodynamic equation (4.25).

Obviously, the errors they found and discussed are due to 1) the approximations of (4.23) they made and 2) due to the implicitly used saturation assumption. The intention of TC, however, was to find an economical and almost accurate method to treat ice in a numerical cloud model. This is why they approximated the exponential terms in (4.29) to avoid costly numerical calculations. In applying θ_{il} in a numerical cloud model TC concluded that the error in using the approximate form of θ_{il} was comparable to those made using conventional irreversible moist thermodynamic approximations. Our emphasis was, however, to understand the physical meaning of the approximations made, especially in relation to entropy. As a result we find that under the general assumptions of a closed adiabatic system, θ_{il} is only conserved if saturation is assumed. We now compare the definition of ice-liquid water equivalent potential temperature θ_{eiv} Eq. (4.29) with the definition of entropy temperature and find, after some algebraic manipulations:

$$\theta_s = \theta_{eiv}\left(\frac{p_0}{p}\right)^{R_0(1/c^*-1/c_{p0})} \exp[(a_{21}r^1 - a_{32}r^3)/c_{p0}T] \times \exp\left\{[(l_{21}+a_{21})r^1 - (l_{32}+a_{32})r^3]\left(\frac{1}{c^*}-\frac{1}{c_{p0}}\right)\Big/T\right\}. \quad (4.36)$$

Following TC we ignore c_2 compared with c_{p0}, and get $c^* = c_{p0} + c_2 r^t = c_{p0}$, and thus

$$\theta_s = \theta_{eiv} \exp[(a_{21}r^1 - a_{32}r^3)/c_{p0}T]. \quad (4.37)$$

This equation clearly shows that θ_{eiv} is identical with θ_s if and only if chemical equilibrium is assumed. This again reflects the two further approximations made by TC in the derivation of θ_{eiv} (and θ_{il}), which together with the first one imply chemical equilibrium. Thus, treating supersaturated conditions with θ_{eiv} or θ_{il} bears an inconsistency in it.

A prognostic equation for θ_{eiv} can be obtained from (3.26) with (4.37) and by neglecting c_2 compared with c_{p0}, which is a straightforward exercise and, therefore, is omitted here.

f. The wet equivalent potential temperature θ_q

Pointin (1984) defined a new temperature θ_q

$$\theta_q = T\left(\frac{p_0}{p^0}\right)^{R_0/(c_{p0}+r^t c_2)} \times \exp\langle\{[l_{21}(T) - R_1 T \ln(p^1/p^{21}(T))]r^1 - (l_{32}(T)+a_{32}(T))r^3\}/T(c_{p0}+r^t c_2)\rangle, \quad (4.38)$$

which the author called the wet equivalent potential temperature. Pointin's definition of wet equivalent potential temperature is an extension of Paluch's (1974) earlier definition which, however, was confined to pure water clouds. Paluch based her definition on the specific entropy and thus already established the strong relationship between entropy and θ_q. In this paper we do not treat her definition of θ_q separately because it is included in the more general definition (4.38). This definition is based on the thermodynamic equation including the ice phase, but no saturation condition is assumed. The system is considered to be open, in contrast to the papers discussed above, and some special forms of external changes were formulated. The discussion of these external changes, however, is beyond the scope of this paper and therefore will be omitted. This is also necessary if the results should be compared with the previous ones, where a closed system was assumed throughout.

Starting again with the Gibbs equation, we find, in the same way as before, the basic thermodynamic equation for a closed adiabatic system including water vapor and ice:

$$\frac{d}{dt}(c_{p0}\ln T) - \frac{d}{dt}(R_0 \ln p^0) + \frac{d}{dt}\left(r^1\frac{l_{21}}{T}\right) - \frac{d}{dt}\left(r^3\frac{l_{32}}{T}\right) + r^1\frac{d}{dt}\left(\frac{a_{21}}{T}\right) - r^3\frac{d}{dt}\left(\frac{a_{32}}{T}\right) + r^t c_2 \frac{d}{dt}\ln T = 0. \quad (4.39)$$

Inserting θ_q in (4.39) we find

$$\frac{d}{dt}(c_{p0}+c_2 r^t)\ln\theta_q = \frac{a_{21}}{T}\frac{dr^1}{dt} - \frac{a_{32}}{T}\frac{dr^3}{dt}. \quad (4.40)$$

Pointin assumes reversibility and neglects the right-hand side and thus finds that $\theta_q^{(c_{p0}+c_2 r^t)}$ is constant.

It can easily be seen that for the system of cloudy air

$$\theta_q = \theta_s. \quad (4.41)$$

Thus, the wet equivalent potential temperature equals the entropy temperature. No additional assumption is made. Therefore θ_q is the most general potential temperature considered so far.

The prognostic equation for θ_q directly follows from (3.26) and (4.41). Although entropy temperature and wet equivalent potential temperature are identical, essential differences of the corresponding prognostic equations have to be stated. Pointin's fundamental thermodynamical equation (1) refers to an open system and includes irreversible processes. To our understanding, however, the only flux through the system's boundaries he considered is a diffusion flux related to the relative motions of the precipitation particles alone, which corresponds to our diffusion flux $\mathbf{J}^2$ or $\mathbf{J}^3$, respectively. Diffusion of water vapor $\mathbf{J}^1$ has not been considered. Pointin studies irreversible condensation as the only irreversible process and ignores the irreversible fluxes of heat momentum, as well as the diffusion flux mentioned before. However, the prognostic equation we presented includes diffusion of all partial masses and the irreversible fluxes of phase change, heat, diffusion and momentum. Diffusion of precipitation

particles and phase changes of water substances, which were the only irreversible fluxes considered by Pointin, presume the existence of precipitation. We stated already in section 3e that θ_s is a constant in a parcel of air if reversibility is assumed, and thus all irreversible fluxes vanish. If diffusion and phase changes are now considered as the only irreversible fluxes, and as they vanish in the absence of precipitation, then obviously it is found that θ_s is conserved in the absence of precipitation, which was one of Pointin's results. It has become clear that Pointin's fundamental thermodynamical equation (1) is a special case of the entropy budget (3.18) or the prognostic equation for θ_s (3.27), respectively.

g. Results

The entropy temperature defined with (3.23) is the most general definition of potential temperatures, and covers all the others potential temperatures. It reduces to

- dry potential temperature θ for dry air,
- moist potential temperature θ_m for moist air if the approximations

$$s^* = s_0{}^0 + s_2{}^0 r^t \approx s_0{}^0 \quad \text{and} \quad c^* = c_{p0} + c_2 r^t \approx c_{p0}$$

are made and the mixing entropies are neglected,
- equivalent potential temperature for a saturated ice-free cloud,
- liquid water potential temperature for a saturated ice-free cloud if the same approximations as in the case of the corresponding differential equation are made,
- ice-liquid water potential temperature for cloudy air if the same approximations as for the corresponding differential relation are made, especially if reversibility is assumed,
- wet equivalent potential temperature for cloudy air.

The entropy temperature as defined by (3.23) is a function of entropy s, the concentrations of dry air m^0 and the total water mixing ratio r^t or total water concentration m^t: $\theta_s = \theta_s(s, m^0, m^t)$. In this sense it can be considered as a measure of entropy and consequently, this holds also for all other definitions of potential temperatures under the respective assumptions.

5. Summary and conclusions

In this paper we demonstrated the use of entropy and its importance in cloud thermodynamics. The budget equation for entropy, as well as the state function were presented and discussed. The budget equations describe the entropy changes in an open system. They allow a clear identification of reversible and irreversible effects. Irreversible processes lead to entropy production, whereas reversible ones do not. The nonnegativity of all entropy sources together represent the essence of the second law of thermodynamics. Gibbs' fundamental equation appears as a powerful tool for deriving the entropy budget, as well as the various forms of thermodynamic equations. Entropy can be expressed as a well-defined function of the thermodynamic variables p, T and m^k, thus establishing a state function. The system on which the formulation of entropy budget as well as state function rely takes into account the existence of water vapor, liquid water and ice. It can also be formulated for other partial masses within the framework developed in this paper.

It must be kept in mind, however, that all physical effects which are related to the existence of individual drops have thus far been ignored. This is not a special feature of the entropy concept, but is a generally accepted assumption of cloud thermodynamics.

Entropy seems to be the most general and also suitable thermodynamical quantity. The motivation for deriving a new thermodynamic equation and defining a new potential temperature comes from the hope of finding a conservative quantity. This paper suggests that entropy is this quantity. The limitations, however, should be clearly expressed. Entropy is produced whenever irreversible fluxes appear. In the author's opinion, a search for further conservative quantities has no physical basis. Entropy can be expressed in terms of a temperature. This entropy temperature covers all known potential temperature definitions under the respective conditions and approximations. It is a major finding of this paper to show that such a general potential temperature can be defined. As the various potential temperatures are special cases of the entropy temperature, which is a measure of entropy, each potential temperature can also be seen as a measure of entropy or at least as an approximate measure of entropy. In conclusion, one can think of the various potential temperatures simply as entropy temperature, or even entropy. All the success reported using one of the potential temperature definitions and applying it to atmospheric processes can also be claimed for the entropy temperature or the entropy. Paluch's (1979) investigation of entrainment in cumli is one famous application of parcel theory and the entropy concept, as she based her definition of wet equivalent potential temperature θ_q on the specific entropy of a parcel of cloudy air and assumed that θ_q is only changed by mixing.

As a by-product of these investigations it was found that the derivation of TC's ice–liquid water potential temperature implicitly assumes equilibrium conditions. Thus an application to supersaturated cases would be inconsistent. The well-known relationship between entropy and entropy temperature allows one to formulate a prognostic equation for the entropy temperature. This prognostic equation includes irreversible effects and holds for an open system. As entropy temperature covers all the other definitions of potential temperature, its prognostic equation offers a tool to derive exact prognostic equations for the various po-

tential temperatures by inserting the respective assumptions. This, however, was not performed for all of the potential temperatures in this paper. The discussion of the prognostic equation for the entropy temperature clearly shows that it is constant in a parcel of cloudy air only if reversibility is assumed. Thus, deviations from a constant value indicate the acting of irreversible fluxes. They can act in two different ways according to the entropy budget; they can produce entropy and some of them can transport entropy through the system's boundaries. Similar arguments also hold for the entropy temperature. Consequently, if entropy temperature or one of the other potential temperatures is used in a numerical cloud model and if it is assumed to be a conserved quantity, it should be stressed that this is only valid if all irreversible fluxes are ignored. Therefore, the errors of this method are at least partially due to the presence of irreversible fluxes. Nothing is said about the magnitude of the errors involved. Referring to Pointin (1984), Tripoli and Cotton (1981) and other references cited in both papers, we assume the error to be in the range of some percent. In general, we expect the transport of entropy by irreversible fluxes to have a greater influence on local change than the entropy production. This, however, will depend on local conditions and also has to be proven by further investigations.

If it is agreed that entropy is the most general thermodynamic variable, it (or entropy temperature) should be used as a model variable in a numerical cloud model. Besides the method just discussed, which is assuming entropy temperature (or any other potential temperature) to be conserved, thus reducing the prognostic variables by one, we can also use either entropy temperature or entropy as a prognostic variable. We prefer entropy because with entropy temperature we run into formal difficulties if no liquid water is present and because the prognostic equation for θ_s is by at least one term more lengthy than the entropy budget equation. Entropy is an extensive quantity and therefore is governed by a budget equation. Thus, all prognostic equations of the model can be formulated as budget equations for extensive quantities and the same numerical techniques can be applied to it. If irreversible effects are included, they have to be parameterized using conventional methods like K-Theory. Thus, the use of the entropy budget should not lead to any problems. If the knowledge of temperature is needed, which is the case in all microphysical models, the entropy state function can be inverted to yield temperature; it only involves a somewhat lengthy exponential calculation. The DFVLR's MESOSCOP model makes use of this entropy concept. First applications of this model are reported by Schumann et al. (1987) (see also Hauf et al., 1984). The usefulness of the entropy concept will be supported by further numerical investigations, especially if entropy is used as a variable in 3-D numerical cloud models.

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APPENDIX

List of Symbols

$d(\cdot\cdot)$	differential change
$d_i(\cdot\cdot)$	internal change
$d_e(\cdot\cdot)$	external change
$\partial(\cdot\cdot)/\partial t$	partial time derivative
$d(\cdot\cdot)/dt$	total time derivative
$D(\cdot\cdot)/Dt$	budget operator
$\nabla(\cdot\cdot)$	gradient operator
$\mathbf{a}\cdot\mathbf{b}$	scalar product
$\mathbf{A}..\mathbf{B}$	double scalar product between tensors
m^0	concentration of dry air ($i = 0$)
m^1	concentration of water vapor ($i = 1$)
m^2	concentration of liquid water ($i = 2$)
m^3	concentration of ice ($i = 3$)
m^t	total water concentration
M^i	partial mass $i = 0, 1, 2, 3$
n^i	mol fractions $i = 0, 1$
r^i	mixing ratio $i = 1, 2, 3, t, 21, 31$
p	pressure
p^0	partial pressure of dry air
p^1	partial pressure of water vapor
p_0	reference pressure (lower index!)
p^{21}	saturation pressure over water
p^{31}	saturation pressure over ice
T	temperature
T_0	reference temperature
θ	potential temperature of dry air
θ_m	potential temperature of moist air
θ_e	equivalent potential temperature
θ_L	liquid water potential temperature
θ_{il}, θ_{eiv}	ice-liquid water potential temperature
θ_e	wet equivalent potential temperature
θ_s	entropy temperature
Ψ	extensive quantity
ψ	mass specific value of Ψ
ψ_i	specific values of Ψ $i = 0, 1, 2, 3$
s	entropy
s^0	zero entropy
s_i^0	specific zero entropies
s^*	specially defined zero entropy
h	enthalpy
μ	Gibbs function
ρ	density
v	specific volumen
l_{ij}	latent heats
a_{ij}	affinities
c_{pi}, c_i	specific heats $i = 0, 1, 2, 3$
$c_p = c_{pn}m^n$	specific heat
c^*	specially defined specific heat
R_i	individual gas constant $i = 0, 1$
$\mathbf{V}$	velocity vector

$\mathbf{V}'$	diffusion velocity $i = 0, 1, 2, 3$
J^i	phase flux $i = 1, 2, 3$
$\mathbf{J}^i$	diffusion flux $i = 0, 1, 2, 3$
$\mathbf{J}^q$	heat flux
$\mathbf{J}_i^q$	inner heat flux
$\mathbf{J}$	momentum flux tensor

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